PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
D01F 1/10, C08K 5/00, C08L 77/00

A1

(11) International Publication Number: WO 94/13870

(43) International Publication Date: 23 June 1994 (23.06.94)

(21) International Application Number: PCT/US93/11576

(22) International Filing Date: 29 November 1993 (29.11.93)

(30) Priority Data:
07/985,426 4 December 1992 (04.12.92) US

(71) Applicant: WARNER-LAMBERT COMPANY [US/US]; 201 Tabor Road, Morris Plains, NJ 07950 (US).

(72) Inventors: WEINRICH, Karl, P.; 5 Munsee Court, Stony Point, NY 10980 (US). HEGGS, Richard, P.; 5776 Tara Hill Drive, Columbus, OH 43017 (US). NORTHRUP, Virginia, M.; 1186 Oakland Avenue, Columbus, OH 43212 (US). PONCE, Enrique, Mejia; Panteon 69-13, Santa Ursula Xitla, Tlalpan, Mexico D.F. 14420 (MX). BALDUCCI, Joseph, J.; 29-41 171st Street, Flushing, NY 11358 (US). WEINSTEIN, Sy; 21 Standish Drive, Glenmont, NY 12077 (US). BARCELON, Shirley, A.; 44 K53 Center Grove Road, Randolph, NJ 07869 (US). RIEGER, Martin; 304 Mountain Way, Morris Plains, NJ 07950 (US).

(74) Agents: ALMER, Charles, W., III; Warner-Lambert Company, 201 Tabor Road, Morris Plains, NJ 07950 (US) et al.

(81) Designated States: AU, BR, CA, JP, KR, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ANTIMICROBIAL TOOTHBRUSH MONOFILAMENT

(57) Abstract

A shaped object such as a toothbrush bristle having an organic antimicrobial agent incorporated therein selected from the group consisting of from about 5 % to about 15 % by weight of an organic antimicrobial compound selected from the group consisting of antimicrobial aromatic acids, antimicrobial esters thereof and antimicrobial phenolic compounds. Methyl paraben may also be added to increase tensile strength and bend recovery.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

ANTIMICROBIAL TOOTHBRUSH MONOFILAMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is directed to antimicrobial compounds incorporated into nylon monofilaments for use as toothbrush bristles and other articles.

2. Description of Related Art

Toothbrushes have been known for many years. Modern toothbrushes are made out of thermoplastic materials and typically have bristles made from an appropriate thermoplastic material such as nylon.

One drawback of toothbrushes is that they can, under the proper conditions of heat and humidity, develop into sources of the very microbial agents that they are used to combat. Others have attempted to control this tendency to contamination by coating the nylon bristles with antibacterial or antimicrobial agents. Coating of the bristles, however, is not generally effective for continued antimicrobial activity, since the coating generally wears off after only a few uses of the toothbrush. After the coating is sufficiently worn to expose part of the underlying fiber, the toothbrush is susceptible to contamination. In addition, coating fibers has the drawback of affecting the

mechanical and handling properties of the filament used to make toothbrush bristles, and many expensive process changes can result from trying to adapt an existing manufacturing operation to antimicrobial coated filament use.

One attempt to incorporate an antimicrobial agent directly into a material for use in batts for mattresses and comforters, various nonwoven fabrics, high pile carpets, socks, interior decorative fabrics, apparel and other similar products has involved incorporation of an inorganic antibacterial agent into polyester. This technique, proposed by Kanebo corporation of Osaka, Japan, impregnates a zeolite, $xMOAl_2O\ ySiO_2zH_2O$, containing a metal ion known to have antimicrobial properties, including silver, copper and zinc. This zeolite is then kneaded in to polyester fiber for various uses using special spinning technology at the spinning stage of a synthetic fiber production process.

The art still has not come up with an adequate antimicrobial toothbrush, or indeed any antimicrobial shaped article, suitable for everyday use that does not require expensive and extensive additional processing steps to be incorporated into a production line for such an object.

SUMMARY OF THE INVENTION

The principal object of the present invention therefore is to provide a monofilament containing an antimicrobial compound capable of providing antimicrobial activity to the toothbrush during use.

It is an additional object of the invention to provide any shaped article used in daily life containing an antimicrobial compound capable of providing antimicrobial activity during use.

Additional objects and advantages of the invention will be set forth in part in the description that follows, and in part will be obvious from this description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

To achieve the foregoing objects and in accordance with the purpose of the invention, as embodied and broadly described herein, the invention provides a material for use as at least part of a shaped object, comprising up to about 10 percent by weight of an organic antimicrobial agent selected from the group consisting of aromatic acids and esters and phenolic compounds.

Additional objects and advantages of the invention will be apparent from considering the claims and description of the inventi n herein.

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to the presently preferred embodiments of the invention.

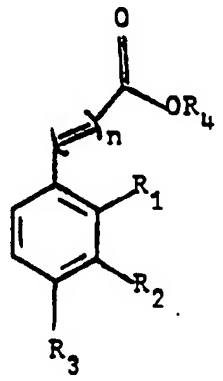
Toothbrush bristles are currently made by extruding nylon monofilaments and attaching premeasured lengths of the monofilaments to the toothbrush handle. It is important that any antimicrobial agent incorporated into the monofilaments affect the process of making the fibers and the final properties of the fibers as little as possible.

Preferably, antimicrobial compounds should be incorporated into a polymer matrix by either extrusion or injection molding in order to render the resulting plastic material antimicrobial. The incorporated material should have a boiling point above 225 degrees C, compatible with nylon or other plastics, and the material must not cause degradation or breakdown of the polymer matrix. About 10% by weight antimicrobial agent is preferred in the monofilament, although the antimicrobial agent can comprise from about 5% by weight to about 15% by weight of the monofilament. Below about 5% by weight, the antimicrobial agent loses full effectiveness and above about 15% by weight the physical properties of the nylon monofilament can suffer.

Two classes of compounds have been discovered that fall

within this category: Group I, aromatic acids and esters; and Group II, phenolic compounds.

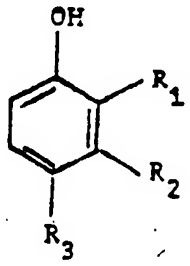
Group I comprises aromatic acids and esters, substituted aromatic acids and esters, conjugated aromatic acids and esters, and substituted conjugated aromatic acids and esters. Compounds having the following structures are preferred:



(I)

wherein R_1,R_2, and R_3 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins or an amino group. R_4 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins. "n" may be 0-3 double bonds.

Group II comprises phenolic compounds. Compounds having the following structure are preferred:



(II)

wherein R_1 and R_2 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins. A preferred example of such a phenolic compound is thymol. R_3 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins or OCH_3. One preferred species of this compound is butylated hydroxy anisole (BHA).

The process for making nylon bristles for toothbrushes comprises the steps of (1) mixing the compounds to be present in the filament, such as thermoplastic materials, mold release agents, plasticizers, lubricants, colorants and other components well known in the art; (2) drying the mixed components if necessary; (3) extruding the components, either to form blended pellets for subsequent processing, or to form the filaments directly; (4) forming the pellets into filaments; (5) drawing the filaments to an appropriate diameter; (6) heat-setting the drawn filaments to set the properties of the filament; (7) winding the filament into a roll for subsequent processing; and (8) wrapping the roll, if necessary, to ship to the assembly point for making the toothbrush.

In practicing the invention, the antimicrobial agent may be added with the plastic material, preferably nylon 6-12, to make the feed material. The mixing should take at least 1 minute to ensure adequate uniformity to the mixture.

The blend should then be dried at 50 degrees C. (122 degrees F) for about 4 hours or down to 0.05% moisture (by weight).

The blend is then transferred to the extruder hopper. The extruder is preferably set to a ratio of 24:1 to 30:1.

The extruder is prepared previously with a low temperature profile in all the zones. For nylon 6-12, the temperatures should be in the range of 200 degrees C to about 230 degrees C. The extruder may be operated with or without pulsations.

The extruder than takes the feed material, conveys it and melts it evenly, compresses it, homogenizes it, and feed the melt under pressure and without pulsations to the filter pack and finally to the monofilament die.

The process then continues with the normal steps and conditions of extrusion of monofilaments with a quenching bath, orientation, heat setting and winding.

One preferred embodiment of the invention is the incorporation of thymol and methyl paraben in combination as an antimicrobial agent in semicrystalline nylon. An unexpected advantage of this combination is that the thymol and methyl paraben in combination increase the tensile strength and the bend recovery of the resultant material.

Although the preferred use of the invention as set forth herein is as a bristle for a toothbrush, the invention may be

used as at least a part of any shaped object that has need for some antimicrobial activity. Examples of such uses include infant toys, plastic utensils, personal care items such as combs and brushes and plastic items used in public places having extensive public physical contact.

Various examples of the invention will now be set forth.

Example 1

10% by weight cinnamic acid was incorporated into nylon 6-12. The nylon pellets had been previously dried to remove all excess moisture. The cinnamic acid powder was fed into a twin screw extruder operating at 234 Degrees C. The resulting pellets were slightly off white in color and exhibited antimicrobial efficacy when tested as shown in Table 1:

Table 1

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

Ph=6 (CFU stands for "Colony Forming Units"

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	$5.5x10^4$	$2.4x10^3$
cinnamic acid 10%	$5.5x10^4$	<100

The pellets were dried at 50 degrees C for four hours and extruded into filaments. The filaments were tested for antimicrobial efficacy and found to be effective.

Example 2

10% by weight methyl anthranilate was incorporated into nylon 6-12. The methyl anthranilate liquid was fed into a twin screw extruder operating at 234 Degrees C. The resulting pellets were slightly off white in color and exhibited antimicrobial efficacy when tested.

The pellets were dried at 50 degrees C for four hours and extruded into filaments. The filaments were tested for antimicrobial efficacy and found to be effective.

Example 3

10% by weight benzoic acid was incorporated into nylon 6-12. The nylon pellets had been previously dried to remove all excess moisture. The benzoic acid powder was fed into a twin screw extruder operating at 234 Degrees C. The resulting pellets were slightly off white in color and exhibited antimicrobial efficacy when tested.

The pellets were dried at 50 degrees C for four hours and

extruded into filaments. The filaments were tested for antimicrobial efficacy and found to be effective.

Example 4 (Comparative Example)

10% by weight phenylacetic acid was incorporated into nylon 6-12. The nylon pellets had been previously dried to remove all excess moisture. The acid powder was fed into a twin screw extruder operating at 234 degrees C. The resulting pellets were slightly off white in color, gave off a terrible odor, and appeared to be degrading in the holding container.

Example 5

A number of tests were carried out using combinations of thymol and methyl paraben as the antimicrobial agent. Pellets were made in accordance with the procedure of Example 1 and tested for antimicrobial activity. Three tests were run at each sample ratio, and the results were averaged, unless a range is indicated in Table 2. The results are set out in Table 2.

Table 2

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=6 (CFU stands for "Colony Forming Units"

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	$1.1x10^5$	$4.1x10^3$
10% thymol, 4% methyl paraben	$1.1x10^5$	$<1.0x10^2$
10% thymol, 2% methyl paraben	$1.1x10^5$	$3.0x10^2$
10% thymol, 1% methyl paraben	$1.1x10^5$	$<1.0x10^2$
8% thymol, 4% methyl paraben	$1.1x10^5$	$2.3x10^2$
8% thymol, 1% methyl paraben	$1.1x10^5$	$<1.0x10^2$

The results show that all treated pellets had antimicrobial activity.

Example 6

In order to confirm that pellets did not lose antimicrobial activity when extruded to form fibers, test runs in accordance with Example 1 were made on fibers with a combination of 10% thymol and 5% methyl-p-hydroxybenzoate. The results are set out in Table 3. Three tests were run for the control and for the antimicrobial fiber, and the results were averaged, unless a range is indicated.

Table 3

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=6 (CFU stands for "Colony Forming Units"

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	9.6×10^4	1.5×10^3
thymol plus methyl-p-hydroxybenzoate	9.6×10^4	$<1.0 \times 10^2$

Example 7

In order to investigate the antimicrobial activities of pellets at neutral pH, several test samples were run using 10% by weight of various antimicrobial agents. The results are set out in Table 4.

Table 4

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=7 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	$1.5x10^5$	$1.4x10^4$
methyl-anthranilate	$1.5x10^5$	$6.8x10^2$
ethyl-anthranilate	$1.5x10^5$	$2.0x10^4$
p-anisaldehyde	$1.5x10^5$	<100
benzylidene acetone	$1.5x10^5$	<100
cinnamic acid	$1.5x10^5$	$1.4x10^2$
BHA	$1.5x10^5$	<100

The results show that antimicrobial activity is observed in all antibacterial agents except ethyl anthranilate.

Example 8

In order to confirm that the antimicrobial agents of the invention did not lose effectiveness upon use, tests of scrubbed fibers were made. The fibers were incorporated into toothbrushes, and the toothbrushes were scrubbed on a test surface for thirty (30) minutes with a 5% dentifrice solution. The results reported in Table 5 are the average of triplicate tests unless a range is indicated. The results show that cinnamic acid withstood scrubbing and still had antimicrobial activity.

Table 5

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=6 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	1.3×10^6	2.5×10^5
cinnamic acid	1.3×10^6	$<1.0 \times 10^2$

Example 9

10% by weight BHA was incorporated into nylon 6-12. The BHA was fed into a twin screw extruder operating at 234 Degrees C. The resulting pellets were slightly off white in color. Fibers were then formed and placed into toothbrushes. The toothbrushes were then scrubbed on a test surface, and the BHA scrubbed fibers still showed antimicrobial activity when tested at pH 7. The results are shown in Table 6 as an average of triplicate samples unless a range is indicated.

Table 6

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=7 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	2.3×10^5	2.3×10^4
BHA scrubbed fibers	2.3×10^5	$<1.0 \times 10^2$

Example 10

10% by weight benzoic acid was incorporated into nylon 6-12. The nylon pellets had been previously dried to remove all excess moisture. The benzoic acid powder was fed into a twin screw extruder operating at 234 Degrees C. The resulting pellets were slightly off white in color and exhibited antimicrobial efficacy when tested as shown in Table 7. Reported values are averages of triplicate tests unless a range is indicated.

Table 7

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=6 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	$5.1x10^4$	$3.8x10^2$
benzoic acid pellets	$5.1x10^4$	$<1.0x10^2$

Example 11

Tests were run to compare the values of scrubbed and unscrubbed toothbrush bristles against fibers that had not been incorporated into toothbrushes. The results are set out in Table 8 and are the average of triplicates unless a range is indicated.

Table 8

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=6 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	6.9×10^5	1.8×10^5
cinnamic acid unannealed fibers	6.9×10^5	$<1.0 \times 10^2$
benzoic acid short fibers	6.9×10^5	2.3×10^2
benzoic acid unscrubbed toothbrush	6.9×10^5	1.2×10^2
benzoic acid scrubbed toothbrush	6.9×10^5	$<1 \times 10^2$, 1.6×10^3, 1.7×10^2

Example 12

Additional tests were run on fibers incorporating methyl anthranilate to determine the effects of processing and scrubbing. The fibers of Example 2 were tested to determine the antimicrobial effect of methyl anthranilate during use. The results are shown in Table 9 as the average of triplicate samples unless a range is noted.

Table 9

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

pH=7 (CFU stands for "Colony Forming Units")

Sample	CFU/ml 0 hrs.	CFU/ml 24 hrs.
Control (untreated)	$1.2x10^5$	$3.1x10^4$
methyl anthranilate short fibers	$1.2x10^5$	$6.8x10^3$
methyl anthranilate unscrubbed toothbrush	$1.2x10^5$	$2.0x10^2$, $1.3x10^2$ $1.8x10^4$
methyl anthranilate scrubbed toothbrush	$1.2x10^5$	$<1x10^2$

Example 13

6% by weight trans-cinnamaldehyde was incorporated into nylon 6-12 that had been previously dried at 170 degrees F, under vacuum. The liquid cinnamaldehyde was blended with pellets made from the nylon, and placed in a jar on a set of rolls to blend before extrusion. The material was then placed in a twin screw extruder operating at 227 degrees C. The resulting blended pellets were light orange in color and exhibited antimicrobial efficacy when tested. The pellets were analyzed for the quantity of cinnamaldehyde and found to be 4.2% cinnamaldehyde by weight of the final pellet.

Example 14

10% by weight trans-cinnamaldehyde was incorporated into nylon 6-12 that had been previously dried at 170 degrees F under vacuum. The liquid was pumped into the extruder downstream of the entrance point of the nylon pellets, so that the liquid was added when the nylon was present in a molten state. The processing temperature was 224 degrees C. The resulting pellets were light orange in color and exhibited antimicrobial efficacy when tested.

The pellets were dried at 50 degrees C for four hours and extruded into filaments. This filament was tested for

antimicrobial efficacy and found to be effective as shown in Table 10. Each value in the table is an average of duplicates unless a range is indicated.

Table 10

Liquid Agitation Assay
Test Organism: Staphylococcus aureus ATCC 6538
(CFU stands for "Colony Forming Units")

Sample	CFU/ml <1 hrs.	CFU/ml 6 hrs.	CFU/ml 10 hrs.
Control (untreated)	$2.6x10^3$	$5.4x10^3$	$6.6x10^3$
Cinnamaldehyde (10%) fibers	$1.9x10^3$	<100	<100

Example 15

To ensure that the antimicrobial effect observed in the other examples was not due to the nylon itself, tests were run to compare the efficacy of nylon as a control against nylon with eugenol and nylon with cinnamaldehyde. The results are shown in Table 11.

Table 11

Liquid Agitation Assay
Test Organism: Staphylococcus aureus ATCC 6538
(CFU stands for "Colony Forming Units")

Sample	CFU/ml 4 hrs.	CFU/ml 24 hrs.
Control nylon	1.6×10^5	1.8×10^4
nylon with eugenol (pellets)	1.3×10^5	<100
nylon with cinnamaldehyde (pellets)	1.3×10^5	5.3×10^3

Example 16

Control tests were run to determine the efficacy of cinnamaldehyde antimicrobial toothbrush filaments over multiple pilot runs to ensure that the observed effects were reproducible outside the laboratory. The results are reported in Table 12.

Table 12

Liquid Agitation Assay

Test Organism: Staphylococcus aureus ATCC 6538

(CFU stands for "Colony Forming Units")

Sample	CFU/ml <1 hrs.	CFU/ml 10 hrs.
Control	6.6×10^4	4.1×10^4
Oral B 40 Toothbrush		
cinnamaldehyde fibers	3.3×10^4	1.0×10^3
cinnamaldehyde fibers (scrubbed)	5.8×10^4	6.5×10^3
cinnamic acid (fibers)	-	6.7×10^2
cinnamic acid (scrubbed fibers)	-	$<1.0 \times 10_2$

Example 17

Thymol and methyl paraben were incorporated into nylon 6-12 at 8% by weight and 1% by weight, respectively. The nylon pellets had been predried for four hours at 175 degrees F before extrusion. The compounding zone of the extruder was run at 224 degrees C. The resulting pellets were dried at 50 degrees C for four hours and extruded into filament. The filament was tensile tested on an Instron apparatus using standard procedures and the bend recovery test was conducted using the British Standard for Bend Recovery Tests on Toothbrush Filament. The resulting fiber had a tensile strength of 92,117 lbs/sq.in. which was an increase in strength of 34.4% over plain nylon filament and the bend recovery was a 62% increase over plain nylon filament.

Example 18

Thymol alone was incorporated into nylon 6-12 at 4 weight percent. The resulting fiber was tested as set out in Example 17. The average tensile strength of this material was 16,509 lbs/sq.in. which was 75.9% less than the nylon control and had a 14% reduction in bend recovery.

The purpose of the above description is to illustrate some embodiments of the present invention without implying a limitation. It will be apparent to those skilled in the art that

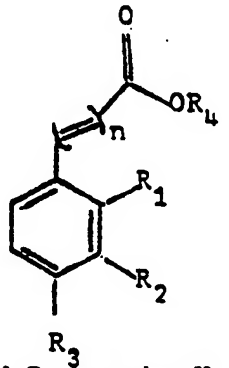
various modifications and variations may be made in the apparatus or procedure of the invention without departing from the scope or spirit of the invention.

We Claim:

1. A monofilament for use as a toothbrush bristle comprising a thermoplastic material and from about 5% by weight to about 15% by weight of an organic antimicrobial compound selected from the group consisting of antimicrobial aromatic acids, antimicrobial esters thereof and antimicrobial phenolic compounds.

2. The monofilament of claim 1, wherein said thermoplastic material comprises nylon.

3. The monofilament of claim 1, wherein said antimicrobial aromatic acid and antimicrobial esters thereof are selected from compounds having the following structure:



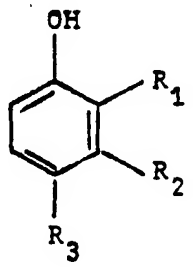
(I)

wherein R_1,R_2, and R_3 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins or an amino group, R_4 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins, and "n" may be 0-3 double bonds, and esters th re f.

4. The monofilament of claim 3, wherein said antimicrobial acid is selected from the group consisting of cinnamic acid and benzoic acid.

5. The monofilament of claim 3, wherein said antimicrobial ester is selected from the group consisting of esters of cinnamic acid and esters of benzoic acid.

6. The monofilament of claim 1, wherein said antimicrobial phenolic compound is selected from compounds having the following structure:



(II)

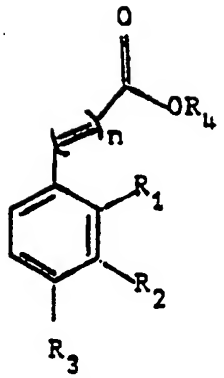
wherein R_1 and R_2 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins, R_3 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins or OCH_3.

7. The monofilament of claim 6, wherein said antimicrobial compound is selected from the group consisting of: thymol, thymol in combination with methyl paraben, thymol in combination with methyl-p-hydroxybenzoate, and BHA.

8. A toothbrush comprising a monofilament bristle, wherein said bristle comprises a thermoplastic material and up to about 10% by weight of an organic antimicrobial compound selected from the group consisting of antimicrobial aromatic acids, antimicrobial esters thereof and antimicrobial phenolic compounds.

9. The toothbrush of claim 8, wherein said thermoplastic material comprises nylon.

10. The toothbrush of claim 8, wherein said antimicrobial aromatic acid and antimicrobial esters thereof are selected from compounds having the following structure:



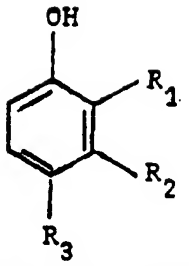
(I)

wherein R_1,R_2, and R_3 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins or an amino group, R_4 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins, and "n" may be 0-3 double bonds, and esters thereof.

11. The toothbrush of claim 10, wherein said antimicrobial acid is selected from the group consisting of cinnamic acid and benzoic acid.

12. The toothbrush of claim 10, wherein said antimicrobial ester is selected from the group consisting of esters of cinnamic acid and esters of benzoic acid.

13. The toothbrush of claim 8, wherein said antimicrobial phenolic compound is selected from compounds having the following structure:



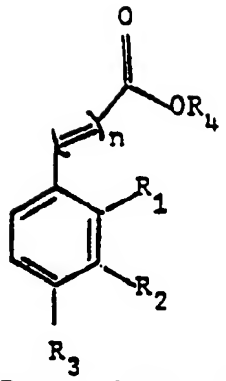
(II)

wherein R_1 and R_2 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins, R_3 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins or OCH_3.

14. The toothbrush of claim 13, wherein said antimicrobial compound is selected from the group consisting of: thymol, thymol in combination with methyl paraben, thymol in combination with methyl-p-hydroxybenzoate, and BHA.

15. A material for use as at least part of a shaped object, comprising from about 5% to about 15% by weight of an organic antimicrobial agent selected from the group consisting of aromatic acids and esters and phenolic compounds.

16. The material of claim 15, wherein said antimicrobial aromatic acid and antimicrobial esters thereof are selected from compounds having the following structure:



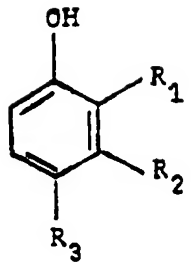
(I)

wherein R_1,R_2, and R_3 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins or an amino group, R_4 may be H, CH_3, C_2H_5, isopropyl, isobutyl, tert-butyl, or higher olefins, and "n" may be 0-3 double bonds, and esters thereof.

17. The material of claim 16, wherein said antimicrobial acid is selected from the group consisting of cinnamic acid and benzoic acid.

18. The material of claim 16, wherein said antimicrobial ester is selected from the group consisting of esters of cinnamic acid and esters of benzoic acid.

19. The material of claim 15, wherein said antimicrobial phenolic compound is selected from compounds having the following structure:



(II)

wherein R_1 and R_2 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins, R_3 may be H, CH_3, C_2H_5, isopropyl, butyl, tert-butyl, or higher olefins or OCH_3.

20. The material of claim 19, wherein said antimicrobial compound is selected from the group consisting of: thymol, thymol in combinatien with methyl paraben, thymol in combination with methyl-p-hydroxybenzoate, and BHA.

21. A thermoplastic material comprising a blend of nylon and methyl paraben.

22. The thermoplastic material of claim 21, further comprising thymol.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 93/11576

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 D01F1/10 C08K5/00 C08L77/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 D01F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,14 94 398 (CHEMWAY CORP.) 23 January 1969 ---	
A	DATABASE WPI Section Ch, Week 9101, Derwent Publications Ltd., London, GB; Class B, AN 91-004868 & JP,A,2 283 312 (SANPO SEIYAKU KK) 20 November 1990 see abstract ---	
A	GB,A,1 276 499 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 1 June 1972 ---	
A	CH,A,570 470 (SANITIZED AG) 15 December 1975 ---	
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
23 March 1994	11. 04. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Tarrida Torrell, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter mal Application No
PCT/US 93/11576

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CH,A,442 736 (AKTIEBOLAGET ASTRA,APOTEKARNES KEMISKA FABRIKER) 31 January 1968 ---	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 398 (C-538)21 October 1988 & JP,A,63 139 937 (MITSUBISHI PETROCHEMICAL COMPANY LIMITED) 11 June 1988 see abstract -----	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 93/11576

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-1494398	23-01-69	NONE	
GB-A-1276499	01-06-72	NONE	
CH-A-570470	15-12-75	NONE	
CH-A-442736		NONE	